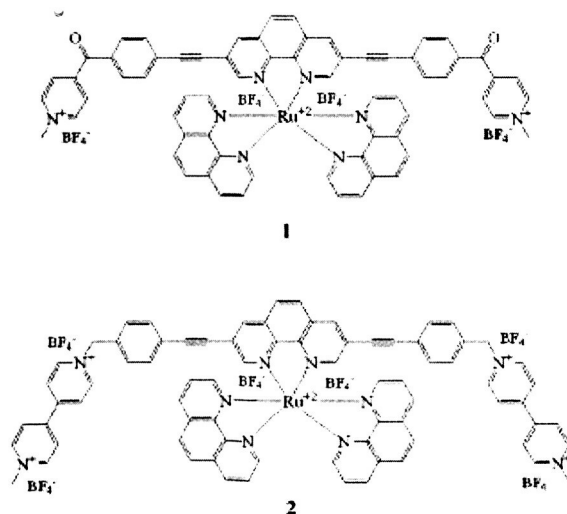


Silica aerogels doped with Ru(II) tris(1,10-phenanthroline)–electron acceptor dyads: improving the dynamic range, sensitivity and response time of sol-gel based optical oxygen sensors

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Complexes **1** and **2** were characterized in fluid and frozen solution and as dopants of silica aerogels. The intramolecular quenching efficiency of pendant 4-benzoyl-*N*-methylpyridinium group (4BzPy) is solvent dependent: emission is quenched completely in acetonitrile but not in alcohols. On the other hand, *N*-benzyl-*N'*-methylviologen (BzMeV) quenches the emission in all solvents completely. The differences are traced electrochemically to a stronger solvation effect by the alcohol in the case of **1**. In frozen matrices or absorbed on the surfaces of silica aerogel, both **1** and **2** are photoluminescent. The lack of quenching has been traced to the environmental rigidity. When doped aerogels are cooled to 77K, the emission shifts to the blue and its intensity increases in analogy to what is observed with Ru(II) complexes in media undergoing fluid-to-rigid transition. The photoluminescence of **1** and **2** from the aerogel is quenched by oxygen diffusing through the pores. In the presence of oxygen, aerogels doped with **1** can modulate their emission over a wider dynamic range than aerogels doped with **2**, and both are more sensitive than aerogels doped with Ru(II) tris(1,10-phenanthroline). In contrast to frozen solutions, the luminescent moieties in the bulk of aerogels kept at 77K are still accessible, leading to more sensitive platforms for oxygen sensors than other ambient temperature configurations.



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